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SCIENCE OF LIGHT

VOLUME 6 NUMBER 2

August

1957

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Published by the

Institute for Optical Research

Tokyo University of Education

in collaboration with

The Spectroscopical Society of Japan

SCIENCE OF LIGHT

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Printed at
Kokusai Bunken Insatsusha
Chiyoda-ku, Tokyo.

On the Iridescence on the Surface of Fishes

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(Received August 24, 1957)

Abstract

The iridescent layer on fish scale is examined with a metal microscope.

Result is that, crystals of guanine are piled up one another with roughly equal interspacings, and the thin film interference of light causes the iridescence.

Analogy between iridescent layer and tactosol[1] is given.

1. Introduction

Many of fishes have a silvery sheen on their scale and skin and some of them give out beautiful iridescence. This silvery sheen is known to be caused by parallel orientation of thin blade-like crystals of guanine. From some kinds of fishes these crystals are collected to prepare pearl essence[2].

The iridescence is, without doubt, related to the orientation of crystals and its origin is studied in the following.

Samples suitable for this study are the scales of Tanago, (*Rhodeus. Ocellatus*), a kind of fresh water fish in Japan. Tanago has on its abdomen a blue sheen and on its head that of greenish yellow. Its scales are easily scraped off from body and crystals of guanine orient themselves on their back nearly parallel to the surface in film form. Scales and skin of herring are also suitable, but because of the difficulty in obtaining a sufficient amount of fresh samples, they were not taken up. Azi (*Trachurus Japonicus*) and Saba (*Sconber Japoncus*), kinds of sea fish have beautiful bright iridescence too, but their sheen layers do not locate on the scales but in the skin underlying the scales. The orientation of the crystals in their skin is rather complicated compared to that on the scales of Tanago or

1) Zocher und Jacobson: Kolloid-Beih B **28**, (1929) 167.
2) Donald Tressler: "*Marine Product of Commerce.*" New York, The Chemical Catalogue Co. Inc. (1923) 782.

herring, but the cause of iridescence seems not to be different.

2. Structure of aggregation of crystals on the scale

A scale was taken off from the fish body by a fine pair of tweezers, put inside out on a glass plate and observed by a metal microscope with 40X objective, as shown in (Fig. 1). Thickness of the aggregation caused the photograph blurred and a sketch (Fig. 2) is appended showing clear boundaries of the crystals.

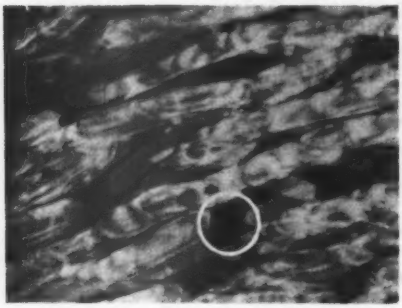


Fig. 1

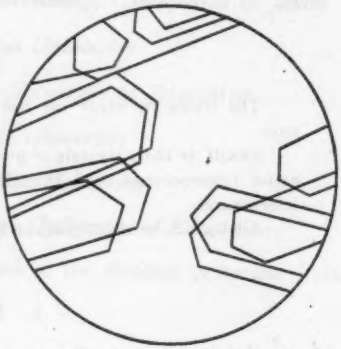
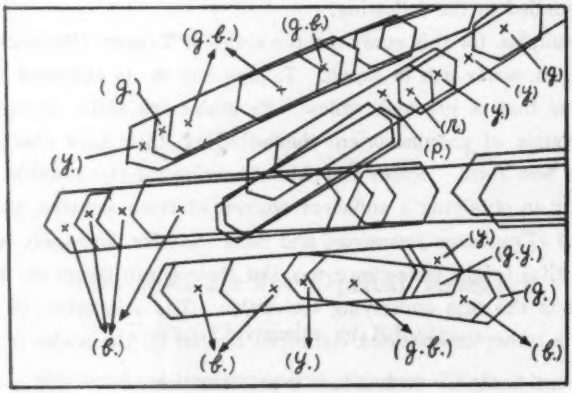


Fig. 2

The crystals line up forming piles of fibrous structure and beautiful mosaic of colors is seen all over the field. (Fig. 3). At outskirts of the aggregation, lines of crystals stretch out and at the vicinity of the ends of lines there are some



(*b.*)—blue, (*g.*)—green, (*y.*)—yellow, (*g. b.*)—greenish blue,
(*r.*)—red, (*p.*)—purple, (*g. y.*)—greenish yellow

Fig. 3

crystals isolated from the aggregation (Fig. 4). These solitary crystals do not give out bright colors but appear almost colorless with white gray at brim and white yellow in the middle which shows that the crystals of guanine are very thin, $(n \times d)$ of which are under 1500 Å. This is the cause of silvery sheen observed on the said aggregation of crystals[3].

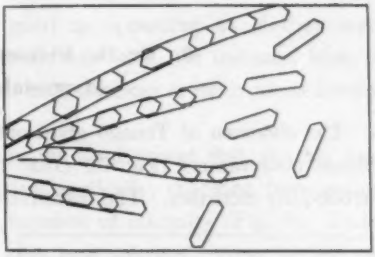


Fig. 4

It is difficult to estimate by casual observation in how many folds the crystals are piled up, but when a scales was left immersed in water for 1–2 hours (the scale was put in a drop of water on a glass plate and covered by a thin glass plate), and observed by a metal microscope; the aggregation of crystals was swollen up and crystals began to crumble.

By the observation in the course of this dissociation the numbers of folds was estimated to be 4–5. By pressing the covering glass slightly several times agitating the water violently, the dissociation was completed and all of the isolated crystals appeared colorless as mentioned before. The colors that had been seen on the aggregation disappeared entirely except in places where the crystals were overlapped (Fig. 5). This proves that the colors seen on the aggregation are not of colored matter but of interference originated by the overlapping of crystals. The size of crystals is roughly 20 $\mu \times 5$ μ.

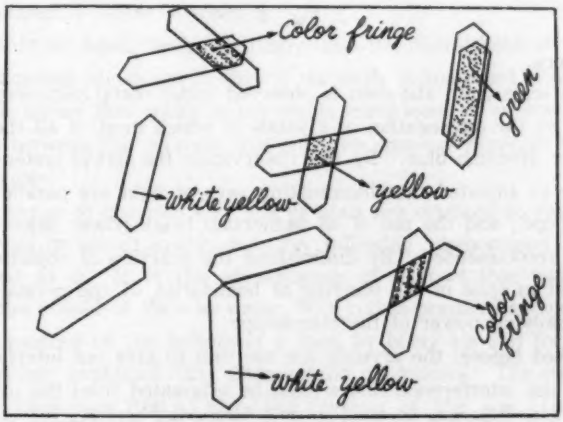


Fig. 5

3) S. Hachisu: Science of Light 6 (1957) 20.

3. On the iridescence of the aggregation of crystals on the scales

The abdomen of Tenago gives out blue sheen when observed normally. By oblique observations (Fig. 6), color changes from blue to red passing purple as the obliquity increases. The transmitted light through the scale tints yellow, the complementary color of blue, when observed by holding it to the light; and the tint varies from yellow to green as the obliquity of scales is increased. This changing of color is the same as observed in the case of thin

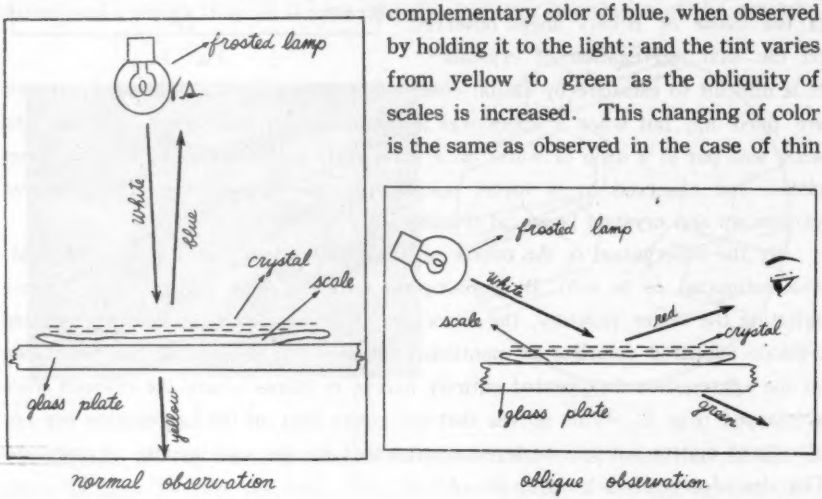


Fig. 6

film interference.

When the scale from abdomen is observed under metal microscope mosaic of colors is seen on the aggregation of crystals in which most of all the specks are colored blue or greenish blue. By this observation the optical system of illumination should be so adjusted that illuminating rays of light are parallel to the axis of the microscope; and the use of oil immersion heigh power objective with iris diaphragm is recommended. By diminishing the aperture of objective the colors become distinct in spite of the blurring of boundaries of the crystals due to the decrease in resolving power of the microscope.

As described before, the crystals are too thin to give out interference colors and therefore the interference colors must be originated from the overlapping of crystals with just adequate interspacings to effect the interference color of blue. By careful observation, the contours of many of the mosaic specks coinside with the those of crystals showing that the colors originate from overlapping of the

crystals. Sometimes two or three crystals piled up appearing as if they were one perfect crystal on which only one color was seen, for instance, blue, or green; but this "single" crystal dissociated into colorless crystals when swollen up with water.

The same can be said of the scales from the head except that in this case the scale gives out orange sheen when observed vertically, changing from orange to greenish yellow passing yellow with the increase of obliquity (Fig. 6). Under a metal microscope the color mosaic is seen predominated by orange and red specks.

Thus, it is concluded that the iridescence of scale is attributed to the interference of light by thin interspacings between blade-like crystals. These interspacings are roughly equally thin all over the aggregation, hence the interference colors coming out of every interspacings are the same, effecting the iridescence visible to the eye.

About the origin of iridescence it could also be infered that the iridescence is due to a diffraction phenomenon by the crystals. But if it were the color by diffraction, it would disappear when the iridescent surface observed under high power microscope as in the case of optical grating.

Further the following fact supports the thin film theory for the iridescence. If a scale is exposed to air, color changes in time

greenish blue → blue → purple → red

on the scale from abdomen, and

orange → yellow → green

on the scale from head, both eventualy lose the distinctness of the color and becomes nondescript bluish gray. But if the scale is immersed in water the color revives. This shows that water is the staple component of substance filling the interspacings between the crystals, and that the spacings diminish with the evaporation of water.

Now it comes to question why the crystals are oriented so regularly. This problem can not be solved easily, but the following phenomenon seems to be closely related to it. It is the phenomenon of tactosol that was observed by Zocher[1] by the colloid of WO_3 in water, WO_3 colloid prepared by special method[1] gives out iridescence on the bottom of a flask by being allowed for a few days to settle. Zocher explained this phenomenon as follows. The colloid particles are very thin (less than 1000 Å) blade-like crystals of the size roughly $1\mu \times 3\mu$, and have electric charge, the particles repulsing one another; thus if the particles settle a regular orientation of particles, in which the interspacings between them are all roughly the same, is effected by the balance between gravity and electric

repulsion acting on every particle.

The crystals of guanine collected from fishes, when refined and suspended in some organic solvent give out interference colors after being allowed for several hours to settle. Namely the pearl essence is a kind of tactosol. Its preparation is as follows: nitrocellulose paste of pearl essence—most of pearl essence are sold in this form, and for the following experiment, the essence made in U. S. A. was most suitalbe—was diluted 5 times as much in buthyl acetate to make a smooth lustrous solution. After the crystals were settled, contaminated liquid was removed by decantation. The proccess was repeated four or five times. The final preparation showed the above described tactosol phenomenon. A small quantity of this conc. preparation giving iridescence on the bottom of flask was transferred by a pipette onto a glass plate and was spread to film by a thin glass rod. After a while the crystals in the film become regularly oriented to reveal interference color patterns. The colors changed as, for instance, green→blue→red→orange, as the solvent evaporated and eventually disappeared. This is due to the diminishing of spacings between crystals effected by evaporation of the solvent. If the solvent was poured onto the discolored film, the color revived in the reverse order, and if the solvent was non-volatile, plasticizer tricresyl phosphate for instance, the color remained stably for a long time. This color film could be made with the said conc. preparation sandwiched between glass plates. With a metal microscope, the color mozaic was observable on this sample in which one color predominated but fibrous structure that was found in the case of fish scale was not seen.

By electrophoresis it was proved that refined crystals of guanine prepared from nitrocellulose paste have negative charge in buthyl acetate. It is of interest that the aggregation of crystals of guanine can reveal iridescent colors without the help of living body, and it seems probable that the regular orientation of crystals found in the epidermis of fishes is caused by the electric charge of compornent crystals.

4. Conclusion

The iridescence on the epidermis of fish is originated by interference of light by thin interspacings in regular orientation of crystals of guanine. This phenomenon resembles closely to that observed with tactosol.

Photoelectric Spectrochemical Analysis for the Trace of Boron in Graphite

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(Received March 16, 1957)

Abstract

Trace of boron in almost pure graphite is determined by means of a "Quantorecorder." The light source is an a. c. arc triggered by a Tesla coil. Using an arc line of carbon as the internal standard line, another arc line of carbon and the resonance line of boron are measured under the discharge condition that the intensity ratio of the above two lines of carbon would take an appropriately chosen value. The working curve so obtained is nearly linear down to boron content of 0.2 ppm, and the reproducibility of measurements is about 4% in standard deviation. Also, various factors which influence the lower limit of determination are discussed.

1. Introduction

Graphite, purified, freed from the trace of boron in particular, is required in quantities as an atomic reactor material. So it is an urgent necessity to establish a method of determining the trace of boron in supposedly pure graphite. At present, a colorimetric measurement using an organic reagent is considered to be a standard method, but it is very laborious and time consuming.

As a rapid method of determining a small ingredient, spectrochemical analysis is considered before everything, and the spectrochemical analysis of the trace of boron in graphite has already been studied by several investigators but their results are at most semi-quantitative. Feldmann and Ellenburg[1] reported lately a quantitative method. After detailed considerations about the various problems encountered in the spectrochemical analysis of boron in graphite, they adopted a d. c. arc method using iridium as an internal standard and a spark method using copper as an internal standard. They reported the lower limits of determination as 0.5 ppm and 0.25 ppm, respectively.

According to their methods, however, the sampling procedures are still fairly laborious and since they use a photographic photometry it is somewhat inferior

1) C. Feldmann and J. Y. Ellenburg: Anal. Chem., **27** (1714) 1955.

as to the rapidity. Now in steel and other metal industries, a direct-reading spectrochemical analysis equipment using a photoelectric photometry, which is named as a "Quantometer," a "Direct Reader" or so, is fairly widely used and is known in its rapidity and reproducibility. If it were possible to determine rapidly by such an equipment the trace of boron in graphite, it would be a very desirable process, since for example, it could then be adopted as a production control method. However, in a photoelectric method of spectrochemical analysis there are some problems that are not involved in the photographic method, and so it will be impossible to adopt the method of Feldmann and Ellenburg as it is. A method suitable with photoelectric equipment was studied and the results are reported here.

It is convenient to classify the samples into two classes:

(a) samples which are nearly perfectly pure, and so the spectrochemical interferences of the co-existent elements can be neglected.

(b) samples which have much ashes, and so the interferences of the co-existent elements must be taken into consideration.

For example, in analyzing raw materials we are in the case of (b), but the problems are so complicated in this case that only the case of (a) will be considered. According to our laboratory experiences, the impurities most frequently found in samples of so-called pure graphites are iron and silicon, and the spectrochemical interference of both elements is negligible except when their contents are very large. Moreover the purification is relatively easy. Hence it will not be meaningless to confine here our consideration to the case of (a).

Feldmann and Ellenburg used iridium or copper as an internal standard, and it is avoided to use another element as an internal standard in this work, for if one adds a certain element as an internal standard to the sample, the sample has to be ground into fine powder and this is not only troublesome but also that the degree of grinding will certainly influence the results of measurement.

2. Theoretical Considerations

In this work a low voltage a. c. arc was used as a light source. It is well known that such an a. c. arc can be considered to be in temperature equilibrium[2]. Now the measured radiation intensity of a spectral line of a source in temperature equilibrium is, as is well known[3],

2) L. S. Ornstein and H. Brinkman: Physica, **1** (797) 1934.
3) W. Finkelnburg und H. Maecker: Elektrische Bögen und thermisches Plasma, Handb. d. Phys., XXII, 1956.

$$I_\lambda = K_\lambda A_\lambda N_0(T) \frac{g}{Z(T)} h\nu \cdot \exp\left(-\frac{E_\lambda}{kT}\right),$$

here h : Planck's constant,
ν : frequency of the spectral line,
g : statistical weight of excited state,
A_λ : transition probability,
$N_0(T)$: number of the atoms,
$Z(T)$: state-sum (Zustandsumme) of the atom,
E_λ : excitation potential of the spectral line,
k : Boltzmann's constant,
T : absolute temperature,
K_λ : coefficient of radiation loss.

The last factor K_λ represents the loss of the line intensity due to self-absorption of the spectral line itself and reflection and absorption of the optical system. This is dependent on the wave-length, the intensity and the energy levels of the spectral line.

In spectrochemical analysis it is the intensity ratio of two spectral lines that is to be considered. The ratio of two spectral lines with wave-lengths λ and λ' is, from the above equation, given by

$$\frac{I_{\lambda'}}{I_\lambda} = \frac{K_{\lambda'}}{K_\lambda} \frac{A_{\lambda'}}{A_\lambda} \frac{Z(T)}{Z'(T)} \frac{N_0'(T)}{N_0(T)} \frac{g'}{g} \frac{\nu'}{\nu} \exp\left(-\frac{E_{\lambda'} - E_\lambda}{kT}\right).$$

If the lines are those emitted by atoms of the same element, $Z'(T)$ and $N_0'(T)$ are equal to $Z(T)$ and $N_0(T)$ respectively, and when a line pair is determined ν'/ν, g'/g, $A_{\lambda'}/A_\lambda$ and $E_{\lambda'} - E_\lambda$ have definite values. Therefore, if one selects lines which show negligible self-absorption and fixes the optical system, the intensity ratio is given by

$$\frac{I_{\lambda'}}{I_\lambda} \propto \exp\left(-\frac{\text{const.}}{T}\right).$$

However in the case of the intensity ratio of two lines which belong to different elements, Z and Z' and N_0 and N_0' do not cancel each other, and the ratio becomes to

$$\frac{I_{\lambda'}}{I_\lambda} \propto \frac{Z(T)}{Z'(T)} \frac{N_0'(T)}{N_0(T)} \exp\left(-\frac{\text{const.}}{T}\right).$$

From the above considerations it can be at once seen that, when the intensity ratio of the appropriate spectral lines of given graphite sample are measured, it will be possible to determine the boron content of the sample by converting the measured ratio of the arc lines BI/CI of boron and carbon to the value in any standard condition of the light source; this conversion will be performed by means of the temperature variation of the light source which can be obtained

from the ratio CI′/CI of the are lines of carbon. But it is practically impossible to compute the values of Z and Z' everytime the temperature changes, and moreover the dependency of N and N' on the temperature change is very complicated and it is impossible to give a quantitative representation of them.

On the contary, if the conditions of the light source, for example the arc current, are adjusted so as CI′/CI will have a definite value which is properly selected and under this condition the value of BI/CI is measured, then the constancy of the conditions of radiation will be, at least in the first approximation, secured even when samples are changed.

Accordingly, one of the arc lines of carbon is applied to the channel for internal standard and the arc lines of carbon and boron are measured. The wavelengths and the line classifications of the lines used are given in Table I.

Table I

Element	Wavelength in A[4]	Lower level[5]	Upper level[5]	Excitation potential in eV
CI	4932.0	$3s\ {}^1P^0_1$	$4p\ {}^1S_0$	10.20
CI	2582.88	$2p^2\ {}^1S_0$	$3s\ {}^3P^0_1$	7.48
BI	2497.733	$2p\ {}^2P^0_{3/2}$	$3s\ {}^2S_{1/2}$	4.94

As a rule in spectrochemical analysis the excitation potential of the standard line shall be as close as possible to that of the line to be determined. But any spectral line of carbon with a favourable excitation potential could not be found and it was unavoidable to use the above lines which have relatively large excitation potentials relative to that of boron. In addition, in place of the above two lines of carbon, other lines with the excitation potential of about six and ten eV were studied, but they were not suitable because of weak intensities or interferences of other lines or bands. The line with wavelength 2478.573 A has the excitation potential of 7.68 eV and is very intense but is considerably self-absorbent[6], and hence is discarded.

3. Experimental Procedure

The equipment used was a "Quantorecorder" of Shimadzu Seisakusho Ltd. Its dispersing equipment is a replica grating of the Bausch-Lomb with 1200 lines/mm and the radius of curvature of 1.5 meter and is mounted in Paschen-Runge type. The number of channels is three including the one for the internal

4) After G. R. Harrison: M. I. T. Wavelength Tables, The Technology Press.
5) C. E. Moore: Atomic Energy Levels I, Circular of N. B. S. 467, 1949.
6) H. Maecker: Z. Physik, **135** (13) 1953.

standard line. The equipped light source can be used as a condensed spark source, a Feussner spark source or a 220 V a. c. arc source triggered by a Tesla coil. Since spark source are relatively inferior in sensitivity, the arc was used throughout this work.

As the standard, several graphite samples of known boron contents were used. Several suitable kinds of practically almost pure graphite were prepared and their boron content were determined by colorimetric method*. The data of the samples used are given in Table II.

Table II

Sample	Boron content in ppm	Remarks
Special	0.1	National Carbon Co.
Regular I	1.1	
Regular II	2.1	
153	0.4	
CB-150	2.7	very fragile

The conditions of measurement were as follows; the width of the entrance slit was 30 μ and that of the exit slits was 50 μ. For the channel of CI 4932 A line a glass plate was inserted between the exit slit and the photo-tube, since the line could be interfered by the second order image of Fe II 2465.914 A. The arc current was 6 Amp. for the sample "Special." The voltages applied to the multiplier photo-tubes were of such values that the integration time for this sample was about twenty seconds under these conditions. The pre-spark time was five seconds. For other samples the conditions except the arc current were held constant and the latter was so adjusted as the value of CI2583/CI4932 would coincide with that of the "Special" within ten per cent. In almost all samples so far measured the value of CI2583/CI4932 depended fairly greatly on the magnitude of the arc current and as was expected from the theoretical reasoning it decreased when the current increased and vice versa. But when the arc current was very large or very small it showed a kind of saturation and did scarecely change with the current. This is perhaps because the intensities of the lines are fairly weak and apt to be interfered by the background light. When the arc current increases definitely the continuous background becomes relatively intense. When the current decreases the condition of the discharge becomes rather spark like and the background increases. In the case of a sample of impure graphite with much ashes, it was sometimes impossible to control the value of CI2583/CI4932 by adjusting the arc current and the value was very large without exception. This is certainly due to the interferences from the co-existent elements. As to the dimensions of the electrodes, samples with a circular section of 5 to 6 mm

* These measurements were done at the fifth division of our Institute.

diameter or a rectangular section of 4 to 8 mm side-lengths were used, and care was not taken to unify the dimensions since the effect of them was not practically appreciable.

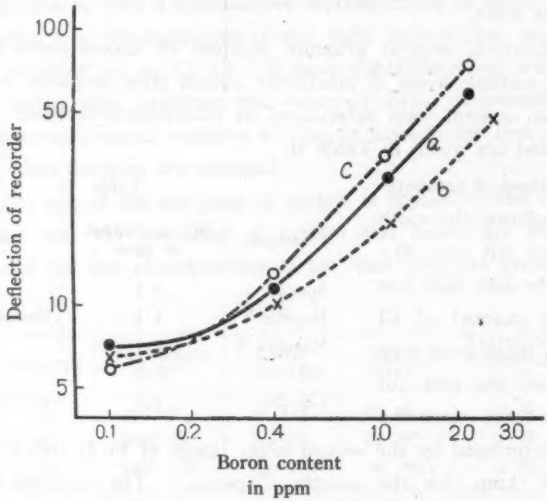

Fig. 1. Working curves obtained in various conditions.

Working curves obtained by the above procedures are shown in Fig. 1. In this place it should be pointed out that the triggering phase of the arc should be held constant, or some errors which are more appreciable in the lower content region will be produced. This is seen by comparing the curves (a) and (b) in the figure. The discharge in (a) was triggered at about $\pi/3$ and $4\pi/3$ of each cycle of line voltage, and that in (b) was at about $2\pi/3$ and $5\pi/3$. Even though the conditions of measurement except the triggering phase were the same for respective samples in both cases, the conditions in arc column would be appreciably different. These facts may be understood from the considerations in 2.

It is seen that a sample whose boron content is above 0.4 ppm can be analyzed with reasonable accuracy by the above method. The reproducibility of the measured data was 3 to 5% in standard deviation. But for a sample with boron content below 0.4 ppm a sufficient accuracy can not be expected.

4. Discussions for the case of lower content

As is well known, the cause of the fact that the slope of the working curve decreases in the region of lower content is that the intensity of the spectral line becomes weak and so the effect of the background becomes dominant. As the

procedures which will make possible to avoid or at least to enfeeble such an objectionable effect, the following can be enumerated:

(a) use of a spectrograph with larger dispersion,

(b) use of a light source which produces weaker background,

(c) use of the so-called line enhancement,

(d) compensation of the background.

Of these methods (a) necessitates another equipment and so will be put out of the question here. Incidentally, it is natural to consider that by using the second order image of the boron line the effect of background can be reduced. Contrary to expectation, the results were very much worse. This is probably because the continuous background is very intense in visible region than in ultraviolet.

In regard to (b), one of the factors which influences the signal to background ratio is known to be the atmosphere of the discharge. Therefore the arcs in the atmosphere of pure argon and the mixtures with several compositions of argon and oxygen were studied. But any desirable results could not be obtained. In the case of pure argon the background decreased definitely but the intensity of the line also decreased, whereas in the mixtures of argon and oxygen the background remained almost unchanged as in air, and in both cases the ratio of the spectral line to its background was not increased.

As for (c), the line enhancement by calcium and aluminum was studied. A hole drilled in the lower electrode sample was packed with a suitable quantity of pure calcium carbonate or alumina, and the spectral lines from the discharge of these samples were measured. The line BI 2498 was considerably enhanced in all measurements, but the discharge was very unstable and any usable data could not be obtained.

In spectrochemical analyses using a photographic photometry it is common to compensate the background effect by subtracting the adjacent background intensity from that of a line. Usually it is impossible to adopt such a procedure in the case of a photoelectric direct analysis, since one cannot discriminate the line intensity and its background in the measured signal. Therefore, unless some device which may make possible to distinguish the desired line intensity from its background be provided with, it is necessary to decrease as far as possible the background light which enters the photo-tube together with the spectral line. In such a photo-electric equipment the exit slits are usually made fairly wide so as the line image should not get out of the slit even when the image be shifted because of temperature variations or so. Assuming that the mechanical construction of the spectrograph is properly designed, the main influence of temperature

disturbance is that due to the variation of grating constant. From the fundamental equation of grating

$$n\lambda = d(\sin\alpha + \sin\beta).$$

the variation of the diffraction angle $\delta\beta$ due to that of the grating constant is given by

$$\delta\beta = -\frac{n\lambda}{d\cos\beta}\frac{\delta d}{d}.$$

Using the values of d, λ, β and $\frac{\delta d}{d}$, the magitude of displacement of image is about 4 μ at 2500 A and 8 μ at 5000 A for one degree of temperature variation. Assuming that tke room temperature changes $\pm 2°C$ at maximum during one course of measurement, a margin width of about 20 μ will be necessary. As the diffraction effect can be neglected for such a slit width, the line intensity will be proportional to the width of entrance slit w, and the background intensity to $w(w+W)$, where W is the margin width of the exit slit. Then the signal to background ratio is given by

$$R = \frac{Aw}{Bw(w+W)+N},$$

where N represents the distortion due to the dark current of the photo-tube, the leakage of the integrating condenser etc. A and B are proportionality constants. N is generally negligible relative to the other terms, so the above relation reduces to the form

$$R = \frac{A}{B}\frac{1}{w+W}.$$

For a given margin width of the exit slit, the narrower the entrance slit, the higher the signal to background ratio.

According to this reasoning, the measurment was repeated using the width of entrance slit of 20 μ and that of exit slits of 40 μ. The result is plotted in the figure, curve c. It will be seen that effect of background is appreciably reduced and the lower limit of determination becomes about 0.2 ppm. In a well temperature-regulated laboratory, it will certainly be possible to attain a better results by using a lower value of the margin width.

As mentioned in the introduction, in this work the analysis of boron in a sample with much ashes was not carried out. One of the reasons, which was not mentioned in the introduction, is that our equipment has only three channels and so there is no room to measure simultaneously the spectral lines of co-existent elements. In the case of a sample which contains much iron, for example, the line BI 2498 A will, as a matter of course, be subjected to the line interference by Fe II 2497.82 A. When there is an extra channel it will be possible

to compensate this interference by measuring simultaneously another line of Fe II, the upper level of which is the same with that of Fe II 2497.82 A, as Feldmann and Ellenburg[1] reported.

5. Acknowledgements

The writer is deeply grateful to Professor Y. Uchida of Kyoto University for his continued encouragement. Grateful achnowledgement is due to President G. Ichinose of our Institute, who gave the writer the opportunity and facility to undertake this work. The writer is greatly indebted to Dr. S. Sengoku, Dr. I. Muraki and Dr. M. Iwata for their valuable advice and discussions during this work. It is a pleasure to express thanks to Miss K. Kosasa for her assistance.

Precise Determination of Nuclear Quadrupole Resonance Line of Solid Iodine

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(Received August 19, 1957)

Abstract

Temperature variations of pure quadrupole coupling constant, eQq_{zz}, and asymmetry parameter, η, of I^{127} in solid iodine are determined by simultaneous measurement of two resonance frequencies corresponding to the transitions $m_z = \pm 1/2 \leftrightarrow \pm 3/2$ and $m_z = \pm 3/2 \leftrightarrow \pm 5/2$. Two oscillators are connected with each other by the sample, and signals of the two resonance frequencies are detected by superregenerative detection at the same time. The errors considered to come from the heating of the sample by several processes, that are related to the character of the oscillator and sample, are completely eliminated by the method used in this experiment. These obtained values suggest that the variations of eQq_{zz} and η should be expressed in terms of the first resonance frequency, ν_1, rather than the apparent temperature. The second resonance frequency, ν_2, has a maximum at 290°K of the value 644.42 Mc and cannot be used as a measure of temperature. Asymmetry parameter is a monotonously decreasing function of the temperature, and eQq_{zz} has a maximum at 200°K of the value 2158.3 Mc. This curve is analysed considering the effect of asymmetry parameter, and calculated values of eQq_0, for an isolated I_2 molecule, decrease normally with temperature. These finally obtained curves can be explained qualitatively by the thermal vibrations of molecules in crystal.

1. Introduction

The nuclear quadrupole coupling constant eQq_{zz} gives many informations regarding the distribution of electron around the nucleus and the deviation of the nuclear charge from spherical symmetry. This constant may also be determined by the hyperfine structure in molecular rotational spectra and by what have been termed direct quadrupole spectra in crystalline solids. Among these methods the pure quadrupole resonance in suitable crystal is a recently developed branch of radio-frequency spectroscopy and has already contributed significant informations on molecular and crystalline structures.

Certain nuclei, such as I^{127}, whose spin is 5/2, has two resonance frequencies ν_1 and ν_2 corresponding to the transitions $m_z = \pm 1/2 \leftrightarrow \pm 3/2$ and $m_z = \pm 3/2 \leftrightarrow \pm 5/2$.

These frequencies are expressed by[1),2)]

$$\nu_1=\frac{3}{20}eQq_{zz}(1+1.09259\eta^2-0.63403\eta^4+\cdots\cdots)$$
$$\nu_2=\frac{3}{10}eQq_{zz}(1-0.20370\eta^2+0.16215\eta^4-\cdots\cdots) \qquad (1)$$

where eQ_{zz} is the quadrupole coupling constant and η is the asymmetry parameter which is expressed by $\eta=(q_{xx}-q_{yy})/q_{zz}$ with respect to the principal axis system of field gradient tensor. These two values eQq_{zz} and η are determined from the two resonance frequencies by the help of Eq. (1).

The pure quadrupole spectrum of I^{127} in solid iodine has been measured by Dehmelt[3)], Pound[4)] and Kamei[5)]. The results are of special interest because of a rather large value of the asymmetry parameter. Townes and Dailey[6)] attemted to explain this asymmetry as arising from the formation of weak intermolecular bonds in the solid, and Robinson, Dehmelt and Gordy[7)] assumed that the bonding orbitals are resonance hybrids formed from a $5s^25p^45d$ configuration and planar arrangement can be more naturally explained.

In both of these explanations the weak intermolecular bonds play an important part to explain the large asymmetry parameter. Therefore it is strongly affected by the temperature owing to the variation in volume. Moreover the quadrupole coupling constant is closely connected with the asymmetry parameter in the above explanations, therefore is also temperature dependent. If this fact alone is taken into consideration, the quadrupole coupling constant should have a positive temperature coefficient. But there has been no report available for discussing the variation of these values. The first aim of this work lies in accurately determining the variation of these values, eQq_{zz} and η. Generally two resonance frequencies have been determined separately by suitable oscillators by measuring the temperature. But the measurement of temperature often involves some errors. In order to eliminate these errors thoroughly, two oscillators are connected with each other by the sample, and two resonance frequencies are detected by these oscillators at the same time.

From these simultaneous measurements, variation of eQq_{zz} and η are accurately determined as a functions of the first resonance frequency ν_1 which act as a substitute for the temperature. When the values of eQq_{zz} and η are plotted

1) R. Bersohn: J. Chem. Phys. **20** (1952) 1505.
2) T. C. Wang: Phys. Rev. **99** (1955) 566.
3) H. G. Dehmelt: Z. Physik **130** (1951) 356.
4) R. V. Pound: Phys. Rev. **82** (1951) 343.
5) T. Kamei: J. Phys. Soc. Japan **7** (1952) 649.
6) C. H. Townes and B. P. Dailey: J. Chem. Phys. **20** (1952) 35.
7) H. Robinson, H. G. Dehmelt and W. Gordy: J. Chem. Phys. **22** (1954) 511.

against observed temperature, it is shown that eQq_{zz} has a maximum at 200°K, while η decreases monotoneously with temperature. The curve of eQq_{zz} is analysed following the two explanations already mentioned, and the constant is converted to that for an isolated I_2 molecule, i.e. eQq_0, then it is found that eQq_0 has no maximum as justly expected from the theory.

2. Apparatus and Procedure of Experiments.

A method of superregenerative detection similar to that described by Dehmelt[3] and Kojima *et al.*[8] is used. Two kinds of spectrometers are arranged for simultaneous measurements. The first which is used for the lower resonance frequency measurement is a push-pull oscillator consisted of tubes 6AF4 with transmission line tuning circuit. The second oscillator is similar to the first except that the miniature tubes are replaced by light house tubes 2C40, and is used for higher resonance frequency detection. These two oscillators are quenched by an oscillator of about 500 kc, the frequency and voltage of which are so chosen as to detect the two resonance signals most sensitively. One end of the transmission line of the first oscillator is connected to an end of the transmission line of the second oscillator (Fig. 1). The sample of about 23 g was placed between the connecting points of the two spectrometers and the two resonance frequencies at the same temperature are simultaneously measured. The two resonance signals are displayed on an oscilloscope through an electronic switch circuit of 25 cycle and using the horizontal sweep of 50 cycle sinewave which is synchronous to the frequency of modulation. A block diagram of the circuit is

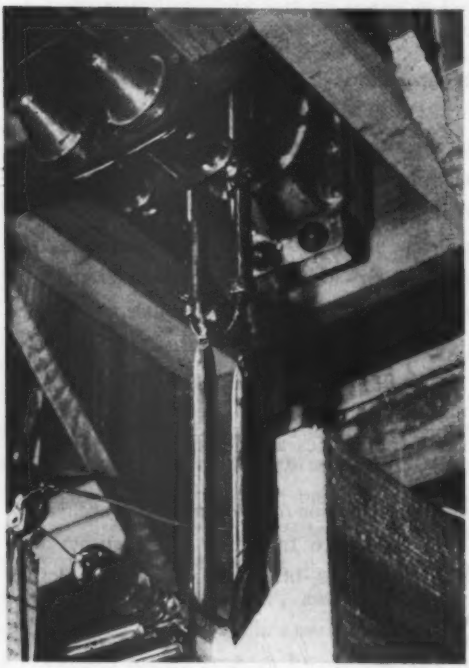

Fig. 1. View of connecting type apparatus.

8) S. Kojima, K. Tsukada, A. Shimauchi and Y. Hinaga: J. Phys. Soc. Japan **9** (1954) 795.

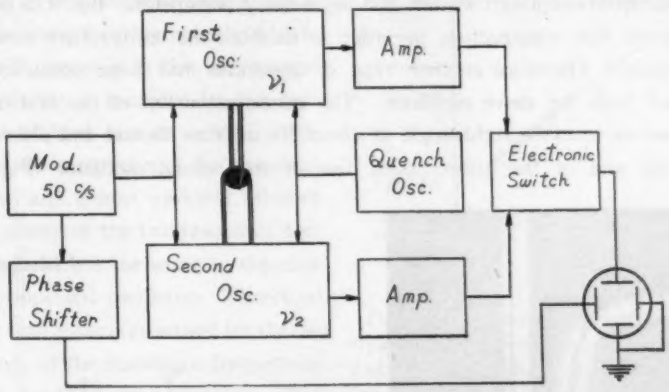

Fig. 2. Block diagram of apparatus.

shown in Fig. 2, and the oscilloscope trace is shown in Fig. 3. The upper curve indicates the ν_1 absorption and the lower shows ν_2 resonance. Because of the large asymmetry parameter of iodine molecule in solid the two oscillators do not interact each other. The resonance frequency is determined by compairing it with the harmonics of a UHF signal generator of the frequency range between 50 Mc to 200 Mc, the generator frequency being immediately measured by an accurate frequency meter of the range from 30 Mc to 500 Mc. But there are some difficulties in determining the resonance frequency precisely because the line shape is often affected by superregenerative detection[9], besides, iodine resonance line has a fine structure[10],[11]. Therefore in order to determine the resonance frequency, the returning trace of the oscilloscope, which is usually made to disappear by the intensity modulation for the convenience of searching for the signals, is displayed for this moment and comparison frequency is determined suitably for both resonance signals in the forward and backward traces.

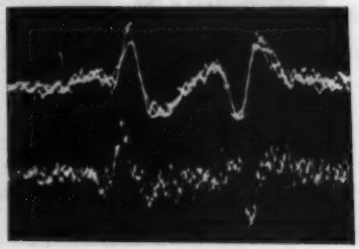

Fig. 3. Oscilloscope trace of the pure quadrupole resonance of I^{127} in solid iodine at room temperature. The upper curve indicates ν_1 absorption and the lower shows ν_2 resonance.

The apparatus described above is useful to determine the correct values of

9) K. Tsukada: J. Phys. Soc. Japan **11** (1956) 956.
10) S. Kojima and K. Tsukada: J. Phys. Soc. Japan **10** (1955) 591.
11) S. Kojima, S. Ogawa, S. Hagiwara, Y. Abe and M. Minematsu: J. Phys. Soc. Japan **11** (1956) 964.

the quadrupole coupling constant and asymmetry parameter. But it is necessary to improve this construction in order to measure the temperature variation of these values. Therefore another type of apparatus has been constructed and compared with the above oscillator. The transmission line of the first oscillator is so bent as to make right angle at about 10 cm from its end and placed parallel to the end of the transmission line of the second oscillator (Fig. 4). A

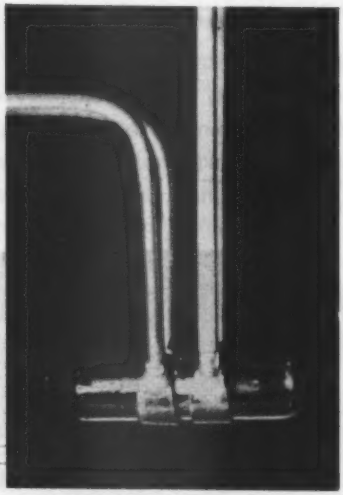

Fig. 4. View of the sample bridged between parallel transmission lines.

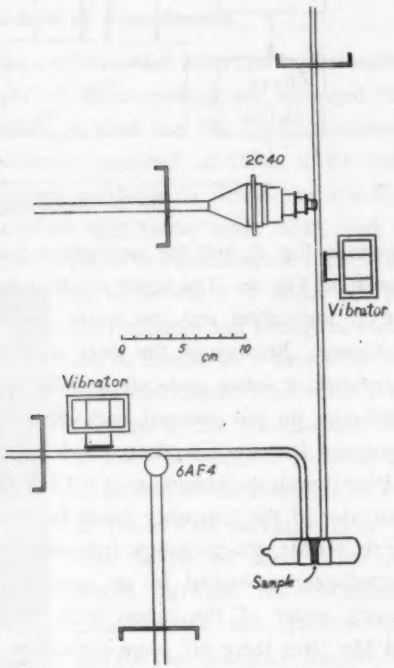

Fig. 5. Dimensions of parallel type apparatus.

sample of about 2 cm in diameter and 2 cm in length is filled in the middle part of a glass tube of 2 cm in diameter, 7 cm in length. It is bridged between the end parts of the parallel transmission lines stretched from the two oscillators. The transmission line of the second oscillator is made longer than its normal length by about a half of the wave length of higher resonance frequency for convenience of cooling the sample (Fig. 5).

The values of η *versus* first resonance frequency at room temperature (35°C~21°C) are plotted in Fig. 6, in which the crosses and circles respectively represent the data measured by using the connecting and parallel type apparatus. It can be concluded from Fig. 6 that both of the apparatus introduce no difference in the results.

Even in one block of sample there might be some local temperature defferences[12], however in this experiment this possibility is excluded by the fact that the bridged sample is small compared to the separation of the transmission lines and almost uiformly affected by the power of the two resonance frequencies, which is the same to the case of the connected oscillator. Therefore parallel type apparatus is used for the observations of the resonance frequencies at low and high temperatures. The experiments at temperatures below the room temperature were performed in petroleum ether cooled by dry ice or in liquid nitrogen, and at higher temperatures with electrically heated bath of vacuum pump oil.

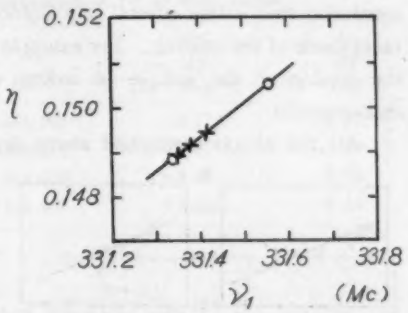

Fig. 6. Asymmetry parameter η of iodine crystal *vs.* the first resonance frequency ν_1. The crosses and circles respectively represent the data obtained by using the connecting and parallel type apparatus.

3. Experimental Results and Discussions

The values of η and eQq_{zz} are accurately determined by simultaneous measurements of the two resonance frequencies of ν_1 and ν_2, because in this method the relation between the two frequencies is derectly obtained without the use of a thermometer or the values of temperature coefficient which is otherwise indispensable.

The values of asymmetry parameter η obtained in this experiment are plotted *versus* temperature in Fig. 7a. The points are remarkably scattered on both sides of a line, which indicates that the errors must have been introduced by the temperature measurement because the values of η themselves have high accuracy. The causes of the errors in the temperature measurement can be imagined as follows. In the process of measurement there are many complicated factors which prevent us from obtaining the true temperature of the sample. Thermal radiation and thermal conduction through the transmission line from the vacuum tubes of the oscillators heat the sample at some parts. Dielectric loss or eddy current in the sample absorbs the oscillating power. It should be noticed that Moss[13]

12) S. Kojima, Y. Abe, M. Minematsu, K. Tsukada and A. Shimauchi: J. Phys. Soc. Japan **12** (1957) 1225.

13) T. S. Moss: "*Photoconductivity in the Elements*" Academic Press, New York, N. Y. (1952).

concluded that iodine crystal is a semiconductor and so the eddy current is the main cause of the heating. For example when the room temperature was 22.7°C, the outside of the sample of iodine was found heated to 34.6°C during the measurement.

All the effects mentioned above depend on the structure, the power and the frequency of the oscillator, as well as on the purity and material of the sample. Therefore it is most probable that even when the thermometer readings are the same, actual temperature of samples are not the same.

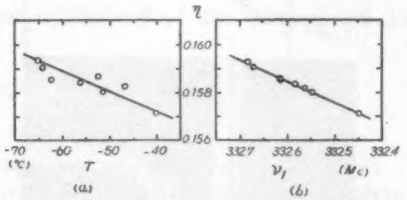

Fig. 7. Asymmetry parameter obtained by the parallel type apparatus *vs.* temperature T, (a), and *vs.* the first resonance frequency ν_1, (b).

In Fig. 7b the values of η that are given in Fig. 7a are plotted against ν_1, which can be regarded as a measure of the temperature, the points lying almost on a straight line. This fact confirms the conclusion described above and suggests the excellence of the simultaneous measurement.

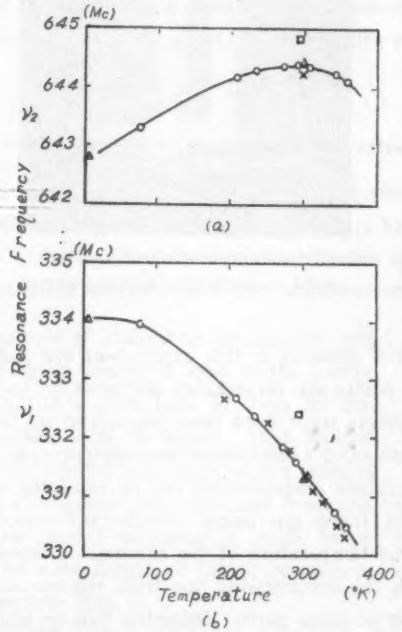

Fig. 8. The resonance frequency of I^{127} in solid iodine *vs.* temperature.
(a) The second resonance frequency, ν_2.
(b) The first resonance frequency, ν_1.
□ Dehmelt; △ Pound; × Kamei;
○ The author

The observed resonance frequencies at four different temperatures are listed in the Table I. The second column shows the temperature on the outside of the sample. For the convenience of comparing with the previously reported values, ν_1 and ν_2 are plotted *versus* temperature in the usual way. All the values obtained this time and reported by Dehmelt[3], Pound[4], and Kamei[5] are shown in Fig. 8, which indicates that the ν_2 curve has a maximum value of 644.42 Mc at 290°K, while ν_1 shows monotonic decrease with rising temperature. Hence ν_2 cannot be used for a measure of the temperature.

From the data listed in Table I constants eQq_{zz} and η can be calculated using Eq. (1). In the evaluation of com-

Table I. Observed resonance frequencies of I^{127} in solid iodine.

No.	Reference Temperature (°K)	ν_1 (Mc)	ν_2 (Mc)	$\frac{1}{\nu_1}\frac{d\nu_1}{dT}$ (10^{-4} deg^{-1})	$\frac{1}{\nu_2}\frac{d\nu_2}{dT}$ (10^{-4} deg^{-1})
1	77	333.941	643.298	−0.17	+0.12
2	208	332.686	644.178	−0.37	+0.08
3	308	331.332	644.336	−0.45	−0.03
4	360	330.475	644.107	−0.52	−0.14

paratively large valnes of η such as in the case of iodine it might be necessary to use the exact expression including the higher powers of η^2 [1),2)]. But actually the values calculated by the use of precise expressions are the same to the values obtained by the use of Eq. (1) within experimental error. Therefore Eq. (1) alone is used to calculate the values of η and eQq_{zz} which are listed in Table II. The values η and eQq_{zz} evaluated from this experiments are plotted in Fig. 9, in which the data reported by Dehmelt, and calculated values from the data reported by Pound are also shown.

Similar to ν_2, eQq_{zz} has a maximum value 2158.3 Mc at 200°K. When η is small enough, the relation among the temperature coefficient of eQq_{zz}, ν_2 and η^2 is given by the following equation[14],

$$\frac{1}{eQq_{zz}}\frac{d(eQq_{zz})}{dT}=\frac{1}{\nu_2}\frac{d\nu_2}{dT}+0.204\frac{d\eta^2}{dT}. \qquad (2)$$

At the maximum values of eQq_{zz} the left hand side of the equation should be zero and then the temperature coefficients of ν_2 and η^2 should be opposite in sign and have suitable values. In Tables I and II these coefficients obtained from the observed data are listed, but their relation is not exactly expressed by Eq. (2) be-

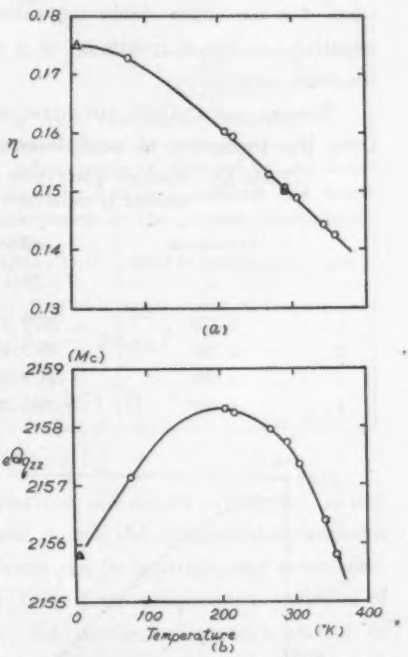

Fig. 9. Quadrupole coupling constant eQq_{zz} and asymmetry parameter η of I^{127} in iodine crystal *vs.* temperature.
□ Dehmelt (value of eQq_{zz} lie outside the figure because of deviation); △ Pound; ○ The author.

14) S. Kojima, A. Shimauchi, S. Hagiwara and Y. Abe: J. Phys. Soc. Japan **10** (1955) 930.

Table II. Nuclear quadrupole couplings of I^{127} in solid iodine.

No.	η	eQq_{zz} (Mc)	$\frac{1}{eQq_{zz}}\frac{d(eQq_{zz})}{dT}$ (10^{-4} deg^{-1})	$\frac{d\eta^2}{dT}$ (10^{-4} deg^{-1})
1	0.1727	2157.12	+0.080	−0.236
2	0.1601	2158.30	−0.005	−0.345
3	0.1488	2157.34	−0.105	−0.345
4	0.1426	2155.81	−0.179	−0.345

cause η is too large. Since the value of the temperature coefficient of η^2 is always negative, ν_2 has a maximum at a temperature higher than that at which eQq_{zz} becomes maximum.

Townes and Dailey[6] attempted to explain this large asymmetry as arising from the formation of weak intermolecular bond. Fractional importance, a, of these resonated bond and the quadrupole coupling constant eQq_0 for an isolated I_2 molecule can be determined uniquely from the observed eQq_{zz} and η. The calculated results obtained from the relations[6),8)] of these values and experimental data in Table II are listed in Table III and Fig. 10, in which eQq_0 is a monotonic decreasing curve with the rise of temperature.

Table III. Nuclear quadrupole coupling constants, eQq_0, of I^{127} for an isolated I_2 molecule calculated from the observed eQq_{zz} and η.

No.	Fractional importance of bond a	eQq_0 $(=(1+\eta)eQq_{zz})$ [6] (Mc)	Fractional contribution $2b$	eQq_0 $(=(1+\eta/3)eQq_{zz})$ [7] (Mc)
1	0.103	2529.25	0.109	2281.30
2	0.097	2503.85	0.101	2273.48
3	0.091	2478.35	0.095	2264.35
4	0.087	2463.23	0.091	2258.28

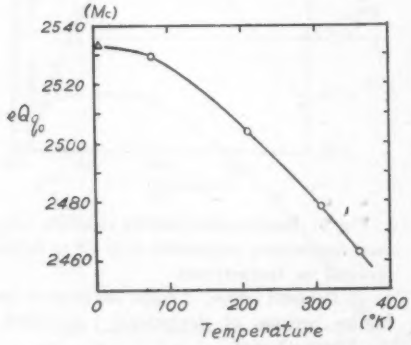

Fig. 10. Temperature variation of the quadrupole coupling constant, eQq_0, of isolated iodine molecule obtained by the model assumed by Townes and Dailey supplemented by the present experimental results.

On the other hand, Robinson, Dehmelt and Gordy[7] assumed the structure B to be consisted of trivalent atoms in the $5s^25p^45d$ configulation forming planar arrangement and to resonate with A containing isolated molecules formed from monovalent iodine atoms in the $5s^25p^5$ configuration. Denoting the fractional contribution of the structure B by $2b$, then

followning relations are obtained,

$$b=\frac{\eta}{3+\eta}$$
$$eQq_0=\left(1+\frac{\eta}{3}\right)eQq_{ax} \qquad (3)$$

The values calculated from the above equations and experimental results are listed in Table III and plotted *versus* temperature as shown in Fig. 11. It also shows a monotonic decreasing curve with the rise of temperature. The Figs. 10 and 11 can be explained by the torsional vibrations of molecules in the crystal[15), 16), 17)].

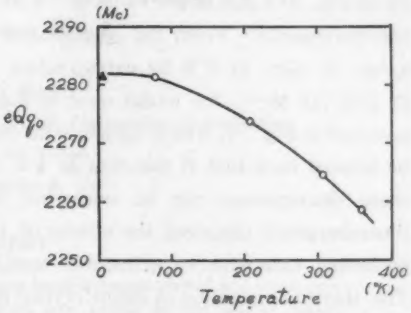

Fig. 11. Temperature variation of the quadrupole coupling constant, eQq_0, of isolated iodine molecule obtained by the model assumed by Robinson, Dehmelt and Gordy supplemented by the present experimental results.

The temperature dependent frequency eQq_0 is to be expressed in the following equation[18)],

$$eQq_0=eQq_{at}\left[1-\frac{3}{8}\frac{h}{\pi^2}\left(\frac{1+\eta/3}{2A_x\nu_x}+\frac{1-\eta/3}{2A_y\nu_y}\right)\right.$$
$$-\frac{3}{8}\frac{h}{\pi^2}\left\{\frac{1+\eta/3}{A_x\nu_x[\exp(h\nu_x/kT)-1]}\right.$$
$$\left.\left.+\frac{1-\eta/3}{A_y\nu_y[\exp(h\nu_y/kT)-1]}\right\}\right] \qquad (4)$$

where eQq_{at} means the eQq value per p-electron and equals to $eQq_{5,1,0}$. ν_x and ν_y are the torsional frequencies, while A_x and A_y are the corresponding moment of inertia. For simplicity I_2 molecule in crystal can be approximated symmetric, then we may put $A_x=A_y$ and $\nu_x=\nu_y$ in Eq. (4). If the temperature variation of eQq_0 as given in Fig. 11 satisfies Eq. (4), the torsional frequency should be 9.11×10^{12} sec^{-1} and the corresponding moment of inertia should be 22×10^{-40} g cm^2. Concerning the torsional frequency, it almost agrees with the value expected from solid state physics, however it seems too large in consideration of the normal vibrational frequency of gaseous iodine molecule being 6.44×10^{12} sec^{-1}. Moreover the moment of inertia estimated from the dimension of the molecule is about thirty five times larger than the above value. This discrepancy is probably due

15) H. G. Dehmelt and H. Krüger: Z. Physik **129** (1951) 401.
16) H. Bayer: Z. Physik **130** (1951) 277.
17) T. Kushida: J. Sci. Hiroshima Univ. Hiroshima, Japan **A. 19** (1955) 327.
18) T. P. Das and E. L. Hahn: "*Nuclear Quadrupole Resonance Spectroscopy*" in "*Solid State Physics*" Academic Press, Inc., New York (in press).

to the large absolute value of temperature coefficient of eQq_0, i. e. $-0.34\times10^{-4}\,\mathrm{deg}^{-1}$. From Fig. 10 a still larger value of $-0.98\times10^{-4}\,\mathrm{deg}^{-1}$ is estimated, which augments the discrepancy. From the smallness of temperature coefficient together with the value of eQq_0 at 0°K by extrapolation being nearly equal to the reported value of 2292.712 Mc[19], the model used in Fig. 11 appears more acceptable than that assumed in Fig. 10, which agrees with Itoh and Kambe's suggestion[20]. It should be noticed here that if the data at 4°K are a little larger than those now adopted, these discrepancies can be somewhat reduced. Recently Kushida, Benedik and Bloembergen[21] theorized the effects of temperature and pressure on eQq_{zz} and presented extensive experimental results in *p*-dichlorobenzene, $KClO_3$ and Cu_2O. The thermal expansion of iodine crystal is reported extremely high, being 250×10^{-6} for the volume coefficient at liquid air temperature and 220×10^{-6} in the range from room temperature to the melting point at 114°C[13]. Therefore the main cause of the discrepancies mentioned above might be the change in volume, and it seems disirable to determine the effect of pressure to the quadrupole resonance frequency of iodine crystal.

4. Acknowledgement

The author wishes to express his sincere thanks to Professor Shoji Kojima for his kind guidance and encouragement throughout this work.

19) V. Jaccarino, J. G. King, R. A. Satten, and H. H. Stroke: Phys. Rev. **94** (1954) 1798.
20) T. Itoh and K. Kambe: J. Phys. Soc. Japan **12** (1957) 763.
21) T. Kushida, G. B. Benedek, and N. Bloembergen: Phys. Rev. **104** (1956) 1364.

Potential Barrier for Proton Transfer in Hydrogen Bond

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(Received August 8, 1957)

Abstract

In infrared studies on the hydrogen bond between phenol and some proton acceptors, two new absorption bands are found in the longer wavelength side of the second overton band of monomolecular phenol O–H stretching vibration. In consequence of considerations about the modifications, due to the hydrogen bonding, of the potential energy curve for the motion of proton, these two bands are, by assuming a double minimum potential as reported in the previous paper[1], explained as due to the association.

By the analogy between the separation of these two bands and the line splittings of the inversion doubling in ammonia, the height of the potential barrier is presumed to be about 20 Kcal./mole.

1. Introduction

For studying the hydrogen bond formation, it appears that infrared absorption spectroscopy has so far been limited almost to the examination of the influences of such bonding on the position[2], intensity[3)-5)] and the like of absorption band corresponding to a specific transition alone. In order to describe about the nature of the hydrogen bond, it seems likely to be important to inquire as to the shape of the potential energy curve for the motion of the bonded hydrogen atom, and this would be succeeded by analyzing systimatically the above-mentioned features, associated with the hydrogen bonding, of absorption bands corresponding to many transitions as possible.

In the previous paper[1], the appearance of two new absorption bands, which were observed in the association between various phenol derivatives and some

1) Y. Sato and S. Nagakura: Science of Light [Tokyo] **4** (1955) 120.
2) Several reviews on hydrogen bonding have been published. L. Keller: Repts. Progr. in Phys. **15** (1952) 1; S. Seki: Chem. and Chemical Ind. **8** (1954) 19.
3) R. Mecke: Disc. Farady Soc. No. 9 (1950) 161.
4) G. M. Barrow: J. Phys. Chem. **59** (1955) 1129.
5) M. Tsubomura: J. Chem. Phys. **23** (1955) 2130; **24** (1956) 927.

proton acceptors through the hydrogen bond, was explained by assuming a potential field consisting of two nearly equal minima for the motion of proton taking part directly in the hydrogen bonding. Recently, in mixtures of water and various oxygenated and nitrogenated solvents two new absorption bands have been observed in the region of 1.46 μ water band[6], both of which have also been attributed to the hydrogen bonding between water and the solvent molecules by their temperature and concentration dependences, as in the case of phenol. Under the above-described circumstances, in order to presume the height of the potential hill[7], the second overtone bands of phenol hydroxyl stretching vibration were measured with some proton acceptors in dilute solutions of carbon tetrachloride. Consequently, some informations about the problems in question seemed to have been derived. Further, the preceding considerations were also applied to the hydrogen bonding between some proton donors and aromatic hydrocarbons.

2. Experimental and Results

Phenol was used as proton donor, and dioxane, acetone, methyl acetate, diethyl ketone, nitromethane and acetonitrile as proton acceptor, as listed in Table 1. Carbon tetrachloride was used as solvent. Some of these substances were purified as follows. Phenol was prepared by drying the purest commercial product over phosphorus pentoxide for several days before being used. Reagent grade acetone was purified by the method of Shipsey and Werner[8], and distilled from phosphorus pentoxide before being used. Methyl acetate was prepared by washing reagent grade with saturated sodium chloride solution, dried with anhydrous magnesium sulfate and distilled. Carbon tetrachloride was purified and dried using the method reported by Harris and Hobbs[9]. The remainder are of the best reagent grade and were used without further purification.

The near infrared grating spectrometer used was constructed in this laboratory particulars of which were described elsewhere[10]. The experiments were made at a room temperature by recording the second overtone bands of phenol hydroxyl stretching vibration in ternary systems consisting of proton donor, proton acceptor and solvent. All the spectral measurements were made in the concentration range of phenol from 0.3 mole/litre to 0.4 mole/litre, in such a concentration no associated

6) To be published; Y. Sato: Science of Light [Tokyo] **5** (1956) 10.
7) Recently, Lippincott and Schroeder semi-empirically suggested the potential energy curves for the motion of proton for ice and oxalyl acid. E. R. Lippincott and R. Schroeder: J. Chem. Phys. **23** (1955) 1099.
8) K. Shipsey and E. A. Werner: J. Chem. Soc. **103** (1913) 1255.
9) J. T. Harris and M. E. Hobbs: J. Am. Chem. Soc. **76** (1954) 1419.
10) Y. Sakayanagi and Y. Sato: Science of Light [Tokyo] **33** (1955) 84.

band of solute molecule itself being apparent. In Fig. 1 (a)~(c), some of the spectral curves obtained are illustrated, in which two new absorption bands are found in the longer wavelength region of the unassociated OH band, and a summary of the wave number shifts of these two bands from the monomolecular phenol hydroxyl absorption band are listed in Table 1.

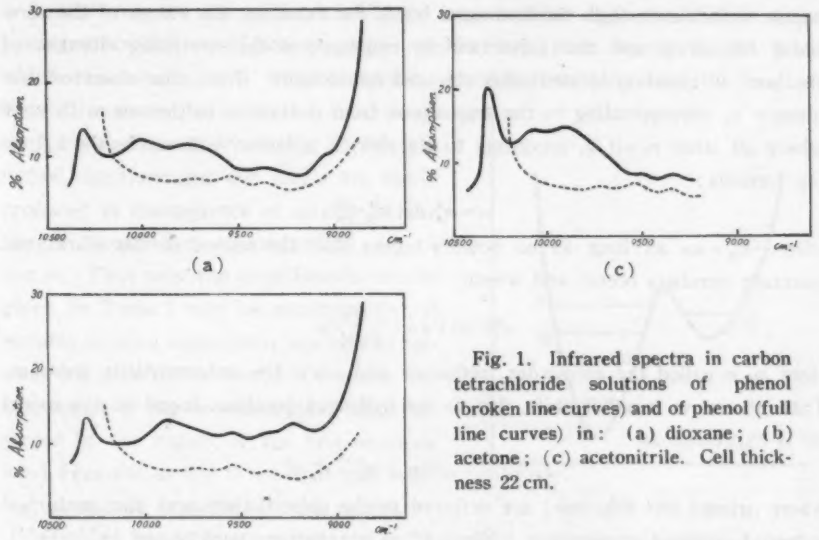

Fig. 1. Infrared spectra in carbon tetrachloride solutions of phenol (broken line curves) and of phenol (full line curves) in: (a) dioxane; (b) acetone; (c) acetonitrile. Cell thickness 22 cm.

Table 1. Proton donors and wave number shifts.

Donor	$\Delta\nu_1$ (cm^{-1})	$\Delta\nu_2$ (cm^{-1})
Dioxane	421	1243
Acetone	433	1091
Methyl acetate	371	1234
Diethyl ketone	499	1134
Nitromethane	175	539
Acetonitrile	247	434

3. Discussions

As the modincation, caused by the hydrogen bond formation, of the shape of the potential energy curve, in which the proton of the unassociated donor molecule is in motion, the following two possibilities may be considered: (a) the first is the case regarded as a simple deviation of only the potential constants from the unperturbed ones at least for the lower energy levels in question, which re-

sults in elongating the bond slightly; (b) the second is the case in which double minimum potential is formed, including, of course, the slight deformation described in (a).

In the model (a), all the constants of the intermolecular potential curve of the donor molecule are more or less perturbed by being associated with the acceptor molecule through the hydrogen bond, for example, the values of the zero-order frequency and the anharmonicity constants of the stretching vibration of the bond in question in particular changed appreciably. Now, the observed frequency ν_i corresponding to the transitions from a state v_i to the one with $v_i=0$ where all other $v_k=0$ is, according to Herzberg's notation[11], shown by the following formula:

$$\nu_i=\omega_i^0\cdot v_i+x_{ii}^0\cdot v_i^2,$$

where $x_{ik}^0=x_{ik}$ as long as no powers higher than the second in the vibrational quantum numbers occur, and where

$$\omega_i^0=\omega_i+x_{ii}+\frac{1}{2}\sum_{i\neq k}x_{ik}.$$

Here ω_i is called the zero-order frequency and x_{ik} is the anharmonicity constant. Then the wave number shift, due to the hydrogen bonding, based on the model (a) is expressed as

$$\Delta\nu_i=(\omega_i^0-\omega_i^{0\prime})v_i+(x_{ii}^0-x_{ii}^{0\prime})v_i^2, \qquad (1)$$

where primed and unprimed are referred to the unperturbed and the perturbed potential constant respectively. Since x_{ii}^0 is a negative quantity and $|x_{ii}^0|<|x_{ii}^{0\prime}|$, the first and the second terms in Eq. (1) are both positive, which results in that the frequency shift for the second overtone band should be more than three times that for the fundamental band.

Let us now consider the case of the hydrogen bonding given in Table 1. As seen in Fig. 1, in the longer wavelength regions of the OH absorption band of monomolecular phenol the two new absorption bands are found, the intensities of which differing considerably with the exception of acetonitril. In the following discussions, at present, only the shorter wavelength absorption bands having the larger intensity will be considered as resulting from the formation of the hydrogen bonding. The low-resolution observation have shown that the shifts, for instance, for acetone and nitromethane are 266 cm^{-1}. and 145 cm^{-1}. respectively for the fundamental vibrations. Then, if the influence of the association on the potential energy curve is limited only to the case of the model (a) the shifts of the second overtone band are anticipated to be at least 700 cm^{-1}. and 400 cm^{-1}.

11) G. Herzberg: Infrared and Raman Spectra, (D. Van Norstrand Company, Inc., New York, 1945).

respectively from Eq. (1). On the other hand, the observed frequency shifts, as given in Table 1, are considerably smaller compared with those expected above, Therefore, the model (a) which is regarded as the simple deformation of the potential curve, would be inapplicable for such a hydrogen bonding. We have now the model (b) to take into considerations. If the second potential minimum is located over the energy level $v_i=3$, the wave number shifts resulting from the nydrogen bonding would become larger as the level rises nearer to the bowl, which also results in a frequency shift. Further, assuming that the bowl is situated midway between the two levels $v_i=2$ and $v_i=3$ as shown in Fig. 2, the perturbed eigenfunctions and levels are newly produced in consequence of mixing of the zero approximation eigenfunctions φ_1, φ_2 and ψ_2. Thus only the experimental results given in Table 1 may be accounted for, if suitable relative separations are located between the unperturbed levels. Of course, the appearance of the two absorption bands observed in the region of the first overtone band, regarded as due to the hydrogen bonding, cannot be explained on this model.

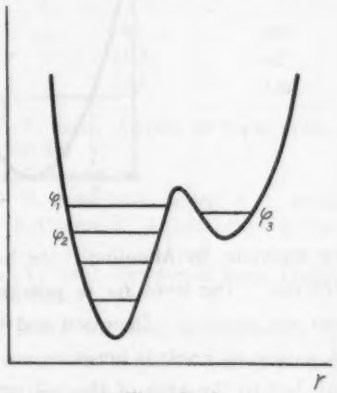

Fig. 2.

Here, it seems that we are obliged to adopt a nearly symmetrical double minimum potential for the phenol-acetone association, as introduced in the previous paper[12]. If it is possible to determine the height of the potential barrier, it seems interesting from the standpoint of the physico-chemistry. For the pur-

Table 2. Separations of the doublet splittings observed with ammonia and the phenol-acetone hydrogen bonding.

Level	Phenol-acetone complex*	NH_3
1	71[a] *	35.7[c]
2	343[b]	312.5[c]
3	658	482[d]

* In these values the separation for the zero-point vibrational level is involved.

a) M. Tsuboi: Private communication [see also Reference (1)].

b) Referen ce (1).

c) H. Y. When g, E. F. Barker and D. M. Dennison: Phys. Rev. 60 (1941) 786 [see also Reference (14)].

d) Reference (11).

12) See reference (1).

pose to infer the height of the trough, the magnitudes of the splittings for vibration ν_2 of the inversion doubling in ammonia[13] are given in Table 2 together with the splittings observed with the phenol-acetone hydrogen bonding. The inversion doubling in ammonia was investigated quantitatively by several workers[14)-17)],

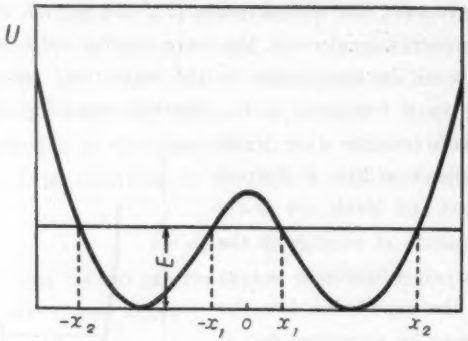

Fig. 3.

for example, by Manning[18] the height of the potential barrier was calculated as 2076 cm^{-1}; the level $2\nu_2$ is just below its top and all higher levels of this vibration are above it. Dennison and Ulenbeck[19] showed that the relative separation of a pair of levels is sensitive not to the particular form assumed for the potential, but to the area of the hill cutt off by the energy level. According to their theory, the difference of the doublet splitting for the nth pair of levels, Δ_n, is expressed by

$$\Delta_n/h\nu = 1/\pi A_n^2, \qquad (2)$$

where

$$A_n = \exp[+(2\pi/h)\int_0^{x_1}[2m(U-E_n)]^{1/2}dx]$$

and

$$\frac{1}{\nu} = \phi dt = 2m\int_{x_1}^{x_2} dx/[2m(E-U)]^{1/2},$$

i. e., ν is the classical frequency of oscillation. Hence, the magnitude of the separation of the two sublevels will increase very rapidly as the top of the potential barrier is approached. Thus it may be allowed to presume, from the

13) D. M. Dennison: Rev. Mod. Phys. **12** (1940) 175.
14) P. M. Morse and E. C. G. Stueckelberg: Helv. Phys. Acta. **4** (1931) 335.
15) D. M. Dennison and G. E. Ulenbeck: Phys. Rev. **41** (1932) 313.
16) M. F. Manning: J. Chem. Phys. **3** (1935) 136.
17) N. Rosen and P. M. Morse: Phys. Rev. **57** (1940) 710.
18) See reference (18).
19) See reference (16).

analogy of the splittings of every levels in these two cases, that the top of the potential hill in question is just above the level $v_i=2$, i. e., the height is about 20 Kcal./mole, since, if the level $v_i=3$ is below the top of the hill, the difference of the doublet splitting of the level is, from the above considerations, expected to be very large compared with the observed value.

The potential energy curve for dioxane, methyl acetate and diethyl ketone appears to be analogous to that for acetone, since their proton accepting powers are nearly equal to that of acetone[20)-22)]. Also for the cases of nitromethane and acetonitrile, though the two potential energy curves are considered to be appreciably asymmetric, almost similar consideration to the above seems to be applicable.

Table 3. Frequency shifts of phenol OH and indole NH stretching vibrations in dilute solutions of benzene.

Level	Phenol	Indole
1	~60	44[c]
2	115[a]	82[d]
3	155[b]	119

a) Y. Sato: Science of Light [Tokyo] 5 (1956) 49.
b) Reference (3).
c) N. Fuson, M.-L. Josien, R. L. Powell and E. Utterback: J. Chem. Phys. 20 (1952) 145.
d) Y. Sato: Science of Light [Tokyo] 6 (1957) 37.

On the loose complexes formed by proton donor molecules with various aromatic hydrocarbons, many investigations have been made[23)]. In Table 3, the frequency shifts for the fundamental, the first and the second overtone bands of phenol hydroxyl and of indole amino stretching vibrations, observed in dilute solutions of benzene and o-xylene, are given. From the table for all the cases exemplified here the frequency shifts for the first and the second overtone bands are appreciably smaller compared with those expected from Eq. (1), yet agreement between them may not be necessarily poor. The higher powers, neglected in Eq. (1), may be necessary to take into consideration for the perturbed vibrational energy, which seems to result partly in the poor correspondences between the observed and the expected frequency shifts. Hence, in these cases the model (a) may likely be conceived up to at least the energy level $v_i=3$, even though the effect of the modification (b) must be, as pointed out above, taken into account, since the energy of an interaction between π-electrons of the aromatic nuclei and the proton appears to be considerably smaller than that of the slightly stretched bond. Accordingly the second minimum is to be located appreciably above the state.

20) W. Gordy and S. C. Stanford: J. Chem. Phys. **9** (1941) 204; W. Gordy: J. Chem. Phys. **9** (1941) 215.
21) S. Nagakura: J. Chem. Soc. Japan **74** (1953) 153; **75** (1954) 734.
22) J. M. Widom, R. J. Philippe and M. E. Hobbs: J. Am. Chem. Soc. **79** (1957) 1383.
23) For instance, L. J. Andrews: Chem. Revs. **54** (1954) 713.

4. Acknowledgements

The author wishes to express his sincere thanks to Profs. Y. Fujioka and H. Ootuka for their interest and encouragement and to Dr. S. Nagakura, University of Tokyo, for his encouragement and valuable advice offered in the present investigation. The author is also indebted to all members of this laboratory for offering their facilities throughout this work.